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**Patentanmeldung Nr.    Patent application No.    Demande de brevet n°**

03100462.5

Der Präsident des Europäischen Patentamts;  
Im Auftrag

For the President of the European Patent Office

Le Président de l'Office européen des brevets  
p.o.

**R C van Dijk**

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LA HAYE, LE

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**Blatt 2 der Bescheinigung**  
**Sheet 2 of the certificate**  
**Page 2 de l'attestation**

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- 1 -

**[ABSTRACT]****New ink compositions for ink jet printing**

5

Radiation curable ink compositions for ink jet printing are disclosed comprising silsesquioxanes.

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**[DESCRIPTION]**

## FIELD OF THE INVENTION

5 The present invention relates to radiation curable ink compositions for ink jet printing containing silsesquioxanes, preferably radiation curable ink compositions comprising radiation curable polyhedral oligomeric silsesquioxanes (POSS).

## 10 BACKGROUND OF THE INVENTION

In the majority of applications printing proceeds by pressure contact of an ink-loaden printing form with an ink-receiving material which is usually plain paper. The most frequently used  
15 impact printing technique is known as lithographic printing based on the selective acceptance of oleophilic ink on a suitable receptor. In recent times however so-called non-impact printing systems have replaced classical pressure-contact printing to some extent for specific applications. A survey is given e.g. in the book  
20 "Principles of Non Impact Printing" by Jerome L. Johnson (1986), Palatino Press, Irvine, CA 92715, USA.

Among non-impact printing techniques ink jet printing has become a popular technique because of its simplicity, convenience and low cost. Especially in those instances where a limited edition of the  
25 printed matter is needed ink jet printing has become a technology of choice. A recent survey on progress and trends in ink jet printing technology is given by Hue P. Le in Journal of Imaging Science and Technology Vol. 42 (1), Jan/Febr 1998, which is hereby included as reference.

30 In ink jet printing tiny drops of ink fluid are projected directly onto an ink receptor surface without physical contact between the printing device and the receptor. The printing device stores the printing data electronically and controls a mechanism for ejecting the drops image-wise. Printing is accomplished by moving the print  
35 head across the paper or vice versa. Early patents on ink jet printers include US 3,739,393, US 3,805,273 and US 3,891,121.

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The jetting of the ink droplets can be performed in several different ways. In a first type of process a continuous droplet stream is created by applying a pressure wave pattern. This process is known as continuous ink jet printing. In a first embodiment the droplet stream is divided into droplets that are electrostatically charged, deflected and recollected, and into droplets that remain uncharged, continue their way undeflected, and form the image. Alternatively, the charged deflected stream forms the image and the uncharged undeflected jet is recollected. In this variant of continuous ink jet printing several jets are deflected to a different degree and thus record the image (multideflection system). According to a second process the ink droplets can be created "on demand" ("DOD" or "drop on demand" method) whereby the printing device ejects the droplets only when they are used in imaging on a receiver thereby avoiding the complexity of drop charging, deflection hardware, and ink recollection. In drop-on-demand the ink droplet can be formed by means of a pressure wave created by a mechanical motion of a piezoelectric transducer (so-called "piezo method"), or by means of discrete thermal pushes (so-called "bubble jet" method, or "thermal jet" method).

Ink compositions for ink jet typically include following ingredients : dyes or pigments, water and/or organic solvents, humectants such as glycols, detergents, thickeners, polymeric binders, preservatives, etc.. It will be readily understood that the optimal composition of such an ink is dependent on the ink jetting method used and on the nature of the substrate to be printed. The ink compositions can be roughly divided in :

- water based ; the drying mechanism involves absorption, penetration and evaporation;
- oil based ; the drying involves absorption and penetration;
- solvent based ; the drying mechanism involves primarily evaporation;
- hot melt or phase change : the ink vehicle is liquid at the ejection temperature but solid at room temperature ; drying is replaced by solidification;
- UV-curable ; drying is replaced by polymerization.

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It will be readily understood that the first two types of ink compositions require a receiving medium that is more or less absorptive. On the contrary, for non-absorbent substrates solvent based inks, hot melt inks or UV-curable inks will be better suited.

5 Early patents on water-based inks include US 3,903,034, US 3,889,269, US 3,870,528, US 3,846,141, US 3,776,742 and US 3,705,043. However, it was recognized early that systems based on water-based inks suffer from a number of disadvantages such as : (a) they require water evaporation and therefore an extensive drying  
10 system, especially when printing speed is important; (b) large printed areas tend to cockle, (c) the images are sensitive to wet and dry rubbing, (d) inks of low viscosity tend to tip dry on the orifice which can be avoided by the use of humectants, usually glycols, which then increase viscosity. The use of polar solvent  
15 based inks can overcome some of the problems inherent to water-based inks, but in its turn causes other problems such as the possible generation of toxic or inflammable vapours. Therefore efforts were conducted to the developmennt of low-solvent ink compositions. In this research the concept of UV-curable ink compositions was  
20 generated, of which a survey is given hereinafter.

An important basic patent on ink compositions for ink jet, satisfying the need for a low solvent content, and containing a UV-curable compound is US 4,303,924. It describes an ink jet printing process using charged droplets wherein the ink composition contains  
25 (a) a multifunctional unsaturated UV-curable compound, (b) a monofunctional unsaturated compound, (c) a reactive synergist, (d) a colorant, (e) an oil soluble salt for conductivity, (f) a photoinitiator, and (g) an organic polar solvent, preferably in a small amount. Several examples of monomers containing acrylate, epoxy, and vinyl functional groups are disclosed.  
30

In EP 0 071 345 a jet ink composition is claimed comprising (A) a cationically polymerizable epoxy resin chosen from particular classes, (B) a photoinitiator, (C) a colorant, (D) a blend of organic solvents.



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In US 4,680,368 a UV-curable ink, not limited to ink jet, is disclosed comprising (A) a poly(urethane-(meth)acrylate), (B) a radically polymerizable compound and (C) a photoinitiator.

According to US 4,978,969 the ink composition comprises 12-80 % of a UV curable adhesive, 3-10 % of a pigment, and 10-40 % of a solvent.

In EP 0 456 039 B1 an ink composition for ink jet is disclosed that is free of volatile organic solvent and contains a colorant, a polar conductive compound, and one or more monomers. In the analogous EP 0 540 203 B1 a non-conductive ink composition, free of volatile solvent, is disclosed, said composition again comprising one or more monomers and a colorant.

In US 5,270,368 the ink composition contains at least two acrylate types, being an aromatic acrylate with carboxyl groups, and an epoxy acrylate.

According to EP 0 658 607 an aqueous ink contains a pigment, a water-soluble resin for dispersing the pigment, a water-soluble UV-curable monomer and a photoinitiator.

In US 5,623,001 an ink is described comprising (a) 20-75 % water, (b) a water-mixable UV-curable compound, preferably an acrylate oligomer, (c) a photoinitiator and (d) a colorant.

According to US 5,641,346 the ink jet ink contains a colorant, a liquid phase comprising water, and an epoxy compound and/or a vinyl ether compound.

In WO 97/31071 a radiation-curable ink jet composition is described comprising from 80% to 95% of a polyfunctional (poly)alkoxylated acrylate monomer.

In US 6,461,419 moisture curable ink jet printable ink compositions are described whereby "curable" means that either reactive silyl groups hydrolyze in the presence of moisture to form compounds having silanol groups that react in the presence of an activated catalyst to form -Si-O-Si- linkages or silanol groups react in the presence of an activated catalyst to form -Si-O-Si- linkages. These moisture-curable compositions cure in the presence of moisture to form crosslinked materials. The moisture is obtained from the atmosphere or from a substrate to which the composition has been applied, although it may be added to the composition.

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Summarizing, a radiation curable ink composition may in general contain one or more radiation curable prepolymers, or oligomers, radiation curable monomers or reactive diluents, optionally one or more photoinitiators, colorants, and other additives. Although  
5 polymerizable monomers are in principle suited for achieving low viscosity, needed in ink jet printing, without introducing a significant amount of water or other solvent, it is a problem to find monomers that are suited for use both in free radically and cationically radiation curable inks.

10 The present invention extends the teachings on radiation curable ink compositions for ink jet.

#### SUMMARY OF THE INVENTION

15 It is an object of the present invention to provide novel radiation curable inks.

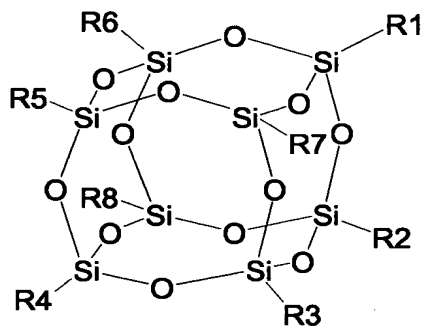
It is another object of the present invention to provide novel radiation curable inks that can be cured radically or cationically. It is a further object of the present invention to provide both free  
20 radically and cationically radiation curable inks for ink jet printing.

These and other objects of the invention will become apparent from the description hereinafter.

25 The above-mentioned objects are realised by providing a radiation curable ink composition comprising one or more silsesquioxanes represented by the following empirical formula  $\text{RSiO}_{1.5}$ , whereby R represents hydrogen, inorganic or any alkyl group, alkylene group, aryl group, arylene group, or organo-functional derivatives of  
30 alkyl, alkylene, aryl or arylene groups.

The above-mentioned objects are preferably realised by providing radiation curable ink compositions comprising one or more radiation curable polyhedral oligomeric silsesquioxanes (POSS) represented by the following empirical formula  $[\text{R}(\text{SiO}_{1.5})]_n$  ( $n=4,6,8,10,12,14,16$   
35 and larger ) that have specific cage structures such as represented by formulae I to III or partial cage structures such as represented by formula IV:

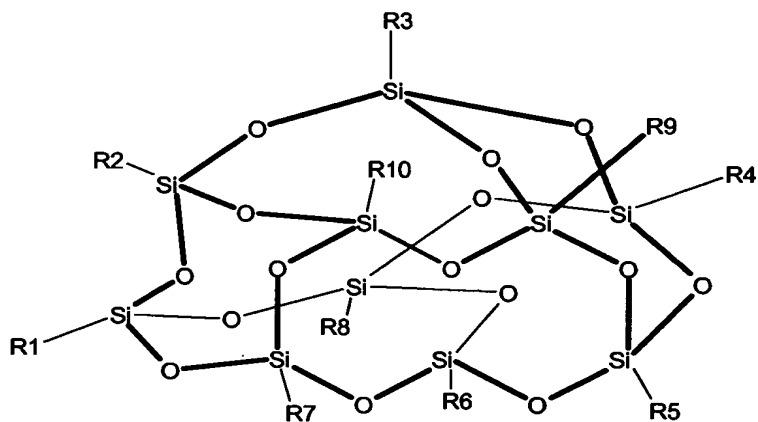
- 7 -



I

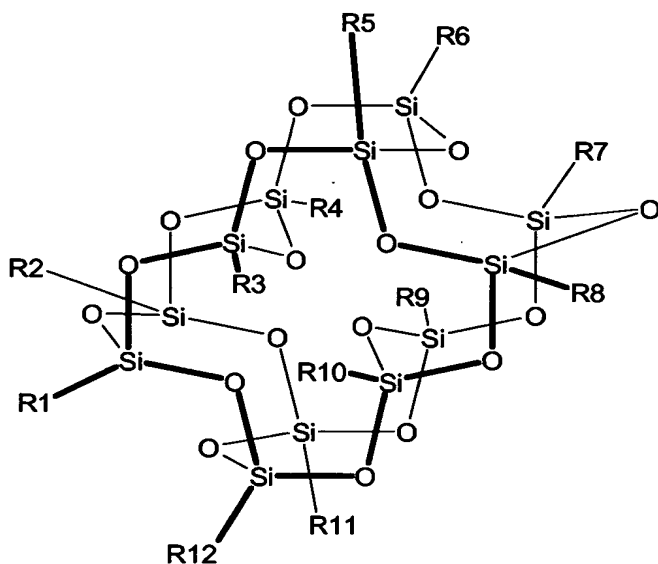
Cage Structure

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II

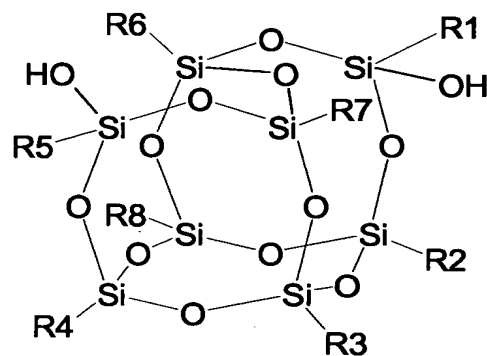
Cage Structure



III

Cage Structure

10



IV

Partial Cage Structure

15

R1 to R12 represent hydrogen as well as inorganic or organic substituents. At least one of the R1-R12 groups comprises a curable functional group. Preferred functional groups are groups such as an

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epoxide, an aziridine, an acrylate, a methacrylate, an acrylamide, a methacrylamide, an olefinic group, a styryl group.

5 DETAILED DESCRIPTION OF THE INVENTION

The structures of silsesquioxanes have been reported as random structure, ladder structure, cage structures and partial cage structures and are discussed in more detail, as well as the  
10 synthesis and the properties of silsesquioxanes, by R. Baney et al. in Chemical Review, 1995, 95, 1409-1430 as well as in the references cited therein and by Guizhi Li et al. in Journal of Inorganic and Organometallic Polymers, Vol. 11 (3), September 2001, page 123-154  
15 as well as in the references cited therein. Silsesquioxanes with specific cage structures have been designated as polyhedral oligomeric silsesquioxanes, POSS. Such cage structures are described in Journal of Inorganic and Organometallic Polymers, Vol. 11 (3), September 2001, page 124, Scheme 1 (structures c-f).

20 Polyhedral oligomeric silsesquioxanes (POSS) have two unique features: (1) the chemical composition is a hybrid, intermediate ( $\text{RSiO}_{1.5}$ ) between that of silica ( $\text{SiO}_2$ ) and silicones ( $\text{R}_2\text{SiO}$ ). (2) POSS molecules are physically large, ranging from approximately 1 to 3 nm. This hybrid (organic/inorganic) composition of POSS technology  
25 enables it to occupy a very unique and dramatically enhanced property space relative to traditional hydrocarbons and inorganics. An important benefit is that it affords the material formulations with excellent thermal, mechanical and oxidative stability, as well as flammability resistance. This is largely due to the inorganic  
30 core of the POSS molecules. The organic portion of their composition provides improved compatibility with existing resins thereby enabling their facile incorporation into conventional plastics. POSS functionalized monomers according to the present invention possess a hybrid inorganic-organic three-dimensional structure which  
35 contains from one to eight reactive organic functional groups. The majority of POSS functionalized monomers contain seven non-reactive organic groups with one unique functionality. By varying

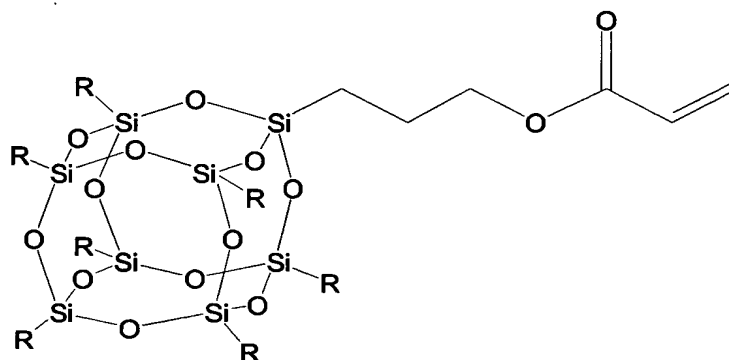
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the functional group and the seven non-reactive organic groups, a multitude of POSS functionalized monomers can be prepared to meet almost any need. While the monofunctional POSS monomers can be incorporated by copolymerization or grafting, multifunctional POSS monomers can be utilized as effective cross-linkers. POSS functionalized monomers react similarly in polymerization, grafting and cross-linking reactions to standard organic monomers. While they react like simple organic monomers, when incorporated into a polymeric material, POSS functionalized monomers impart significant improvements in the thermal, mechanical, and gas separation properties of traditional plastics.

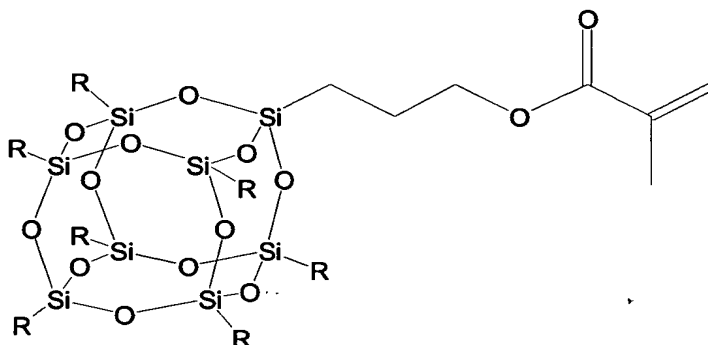
Silsesquioxanes (POSS) according to the present invention are commercially available from companies such as Hybrid Plastics, Fountain Valley, CA 92708-6117, USA.

Representative examples of compounds corresponding to general formulae I to IV are listed in the following Table 1 without being limited thereto. Compared to the state-of-the-art acrylates and methacrylates used in UV curable inks, the compounds according to the present invention have at least one extra functionality introduced into the molecule, offering new opportunities for ink formulation and for printing on non-absorbent substrates such as metal and ceramic surfaces.

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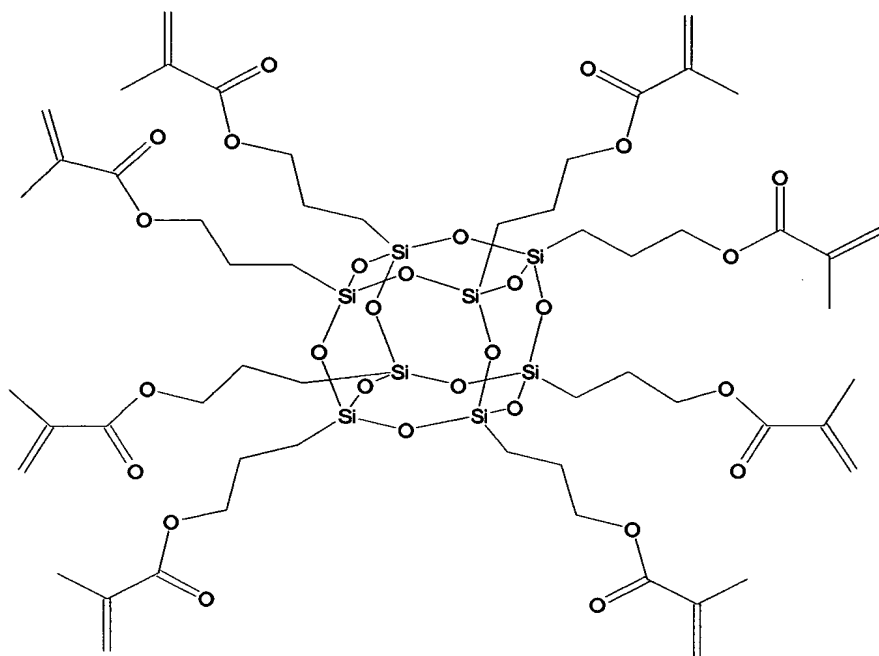
Table 1

- I. 1                    R = cyclohexyl  
I. 2                    R = cyclopentyl  
I. 3                    R = isobutyl

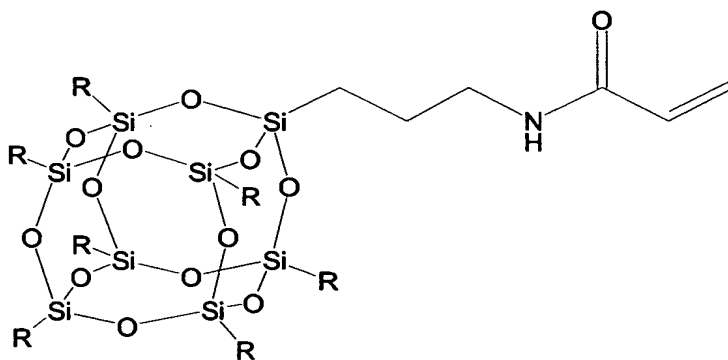


- I. 4                    R = cyclohexyl  
I. 5                    R = cyclopentyl  
I. 6                    R = ethyl  
I. 7                    R = isobutyl  
I. 8                    R = isooctyl  
I. 9                    R = phenyl

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I. 10

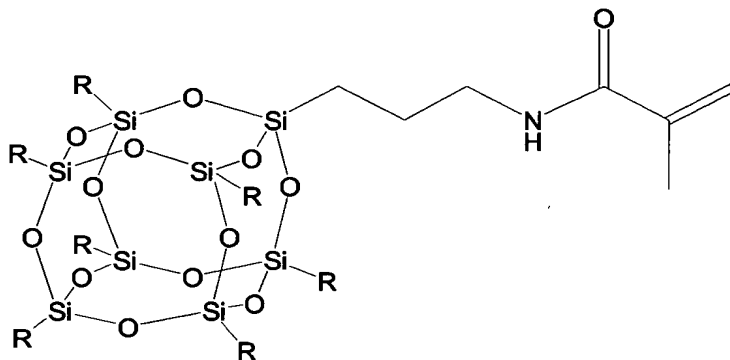


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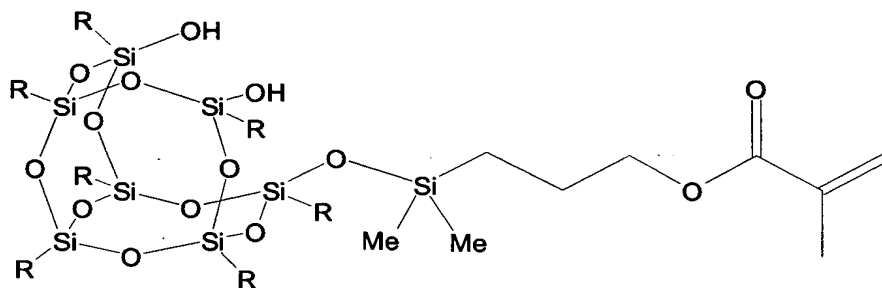
- |       |                 |
|-------|-----------------|
| I. 11 | R = cyclohexyl  |
| I. 12 | R = cyclopentyl |
| I. 13 | R = isobutyl    |

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- 12 -



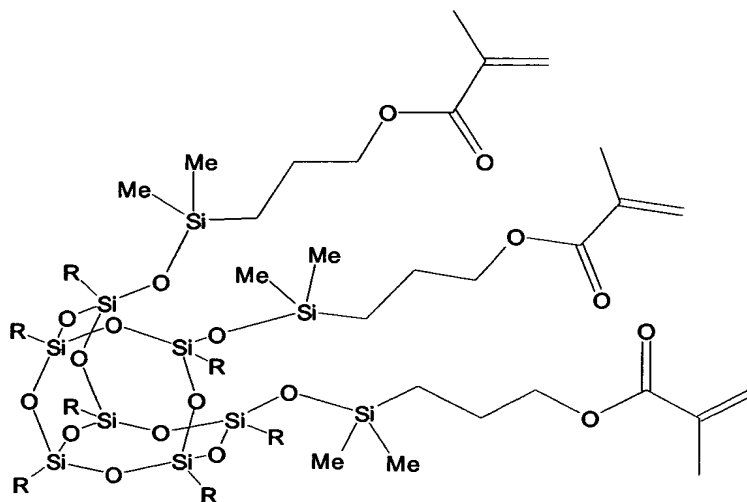
- I. 14                      R = cyclohexyl  
I. 15                      R = cyclopentyl  
I. 16                      R = ethyl  
I. 17                      R = isobutyl  
I. 18                      R = isooctyl  
I. 19                      R = phenyl



- I. 20                      R = cyclohexyl  
I. 21                      R = cyclopentyl  
I. 22                      R = isobutyl



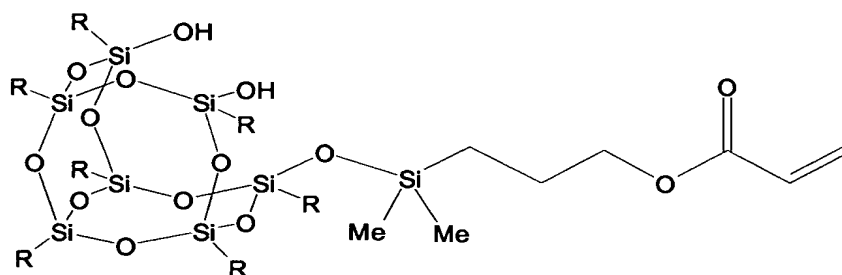
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I. 23                      R = cyclohexyl

I. 24                      R = isobutyl

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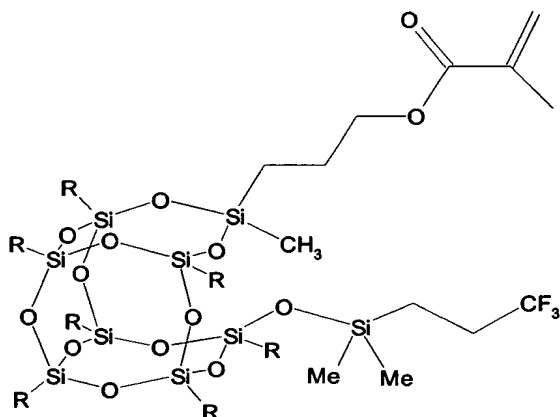
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I. 25                      R = cyclohexyl

I. 26                      R = cyclopentyl

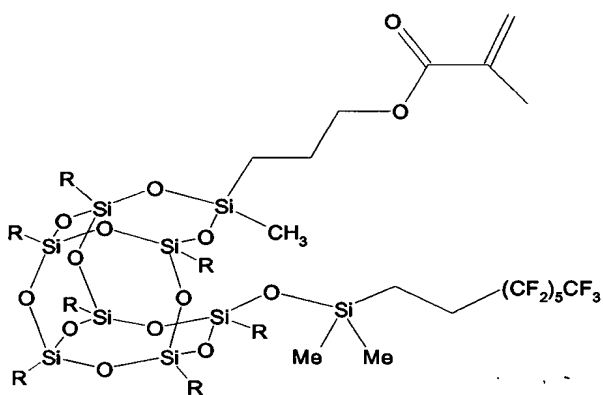
I. 27                      R = isobutyl

- 14 -



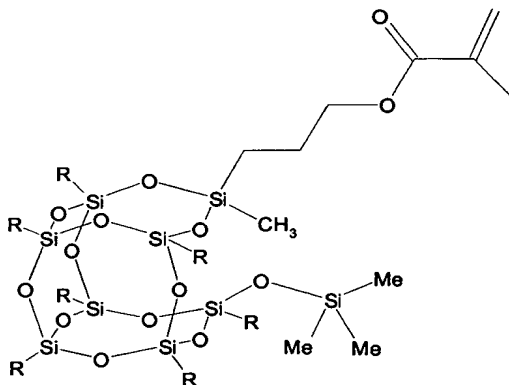
I. 28

R = cyclopentyl



I. 29

R = cyclopentyl



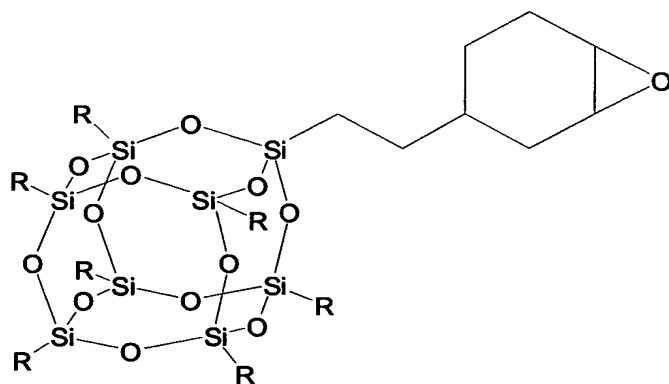
I. 30

R = cyclopentyl

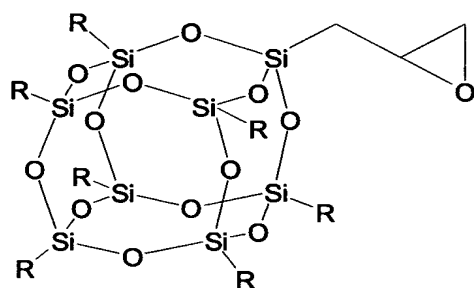
I. 31

R = isobutyl

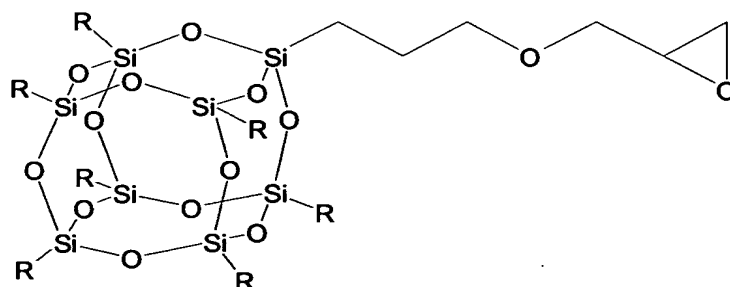
- 15 -



- I. 32                      R = cyclohexyl  
I. 33                      R = cyclopentyl  
I. 34                      R = isobutyl

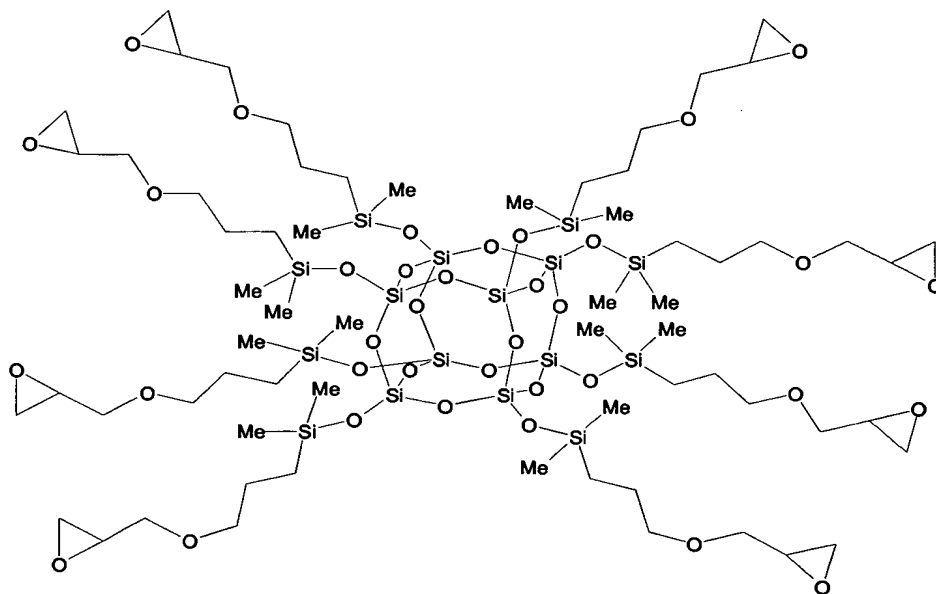


- I. 35                      R = cyclohexyl  
I. 36                      R = cyclopentyl  
I. 37                      R = isobutyl

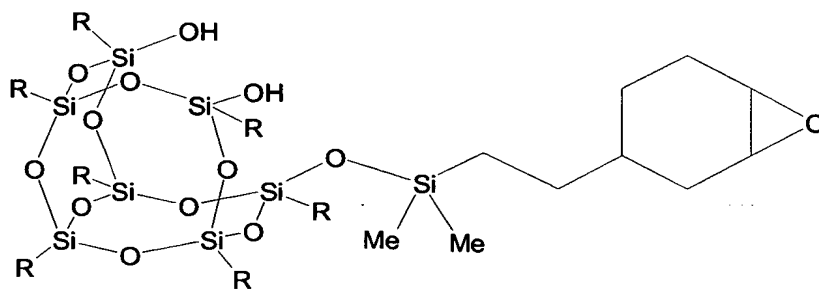


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- I. 38            R = cyclohexyl  
I. 39            R = cyclopentyl  
I. 40            R = isobutyl  
I. 41            R = ethyl  
I. 42            R = isooctyl  
I. 43            R = phenyl

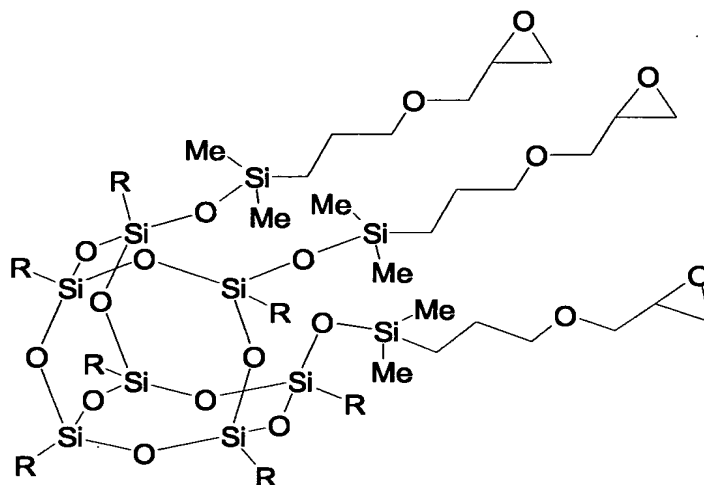


I. 44

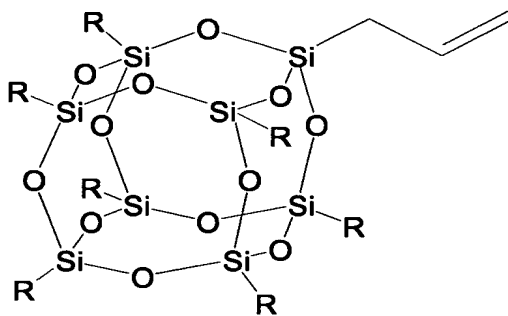


I. 45            R = isobutyl

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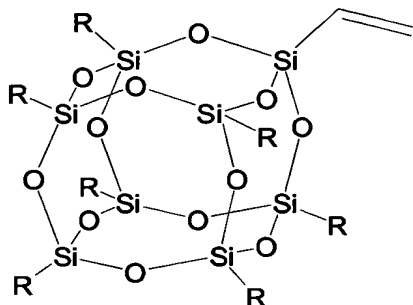


- I. 46                      R = cyclohexyl  
 I. 47                      R = cyclopentyl  
 I. 48                      R = isobutyl  
 I. 49                      R = ethyl



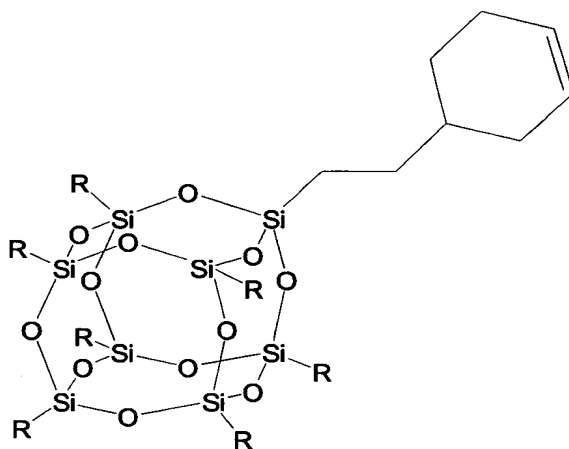
- I. 50                      R = cyclohexyl  
 I. 51                      R = cyclopentyl  
 I. 52                      R = isobutyl

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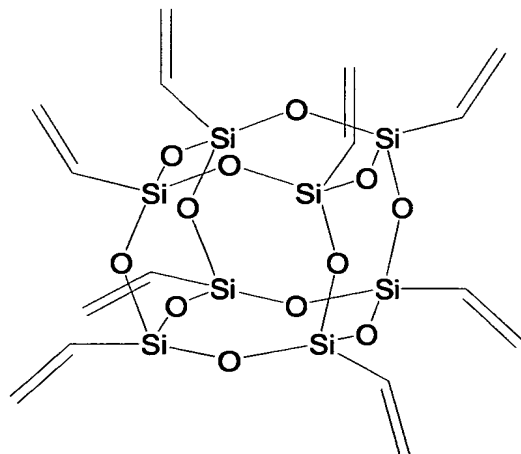


- I. 53                      R = cyclohexyl  
I. 54                      R = cyclopentyl  
I. 55                      R = isobutyl

5



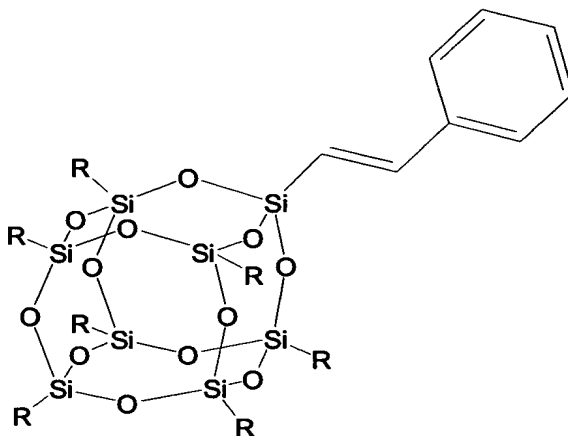
- I. 56                      R = cyclopentyl



- I. 57

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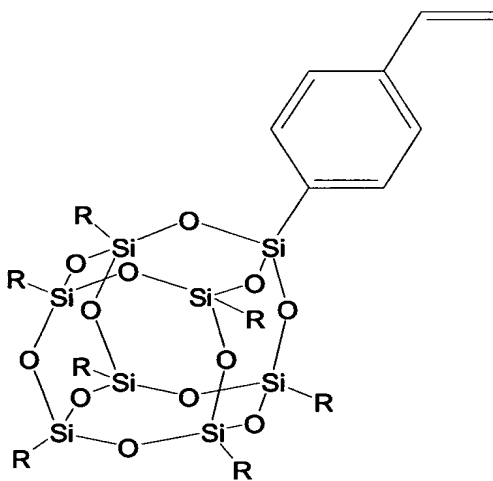
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I. 58

R = isobutyl

5



I. 59

R = cyclohexyl

I. 60

R = cyclopentyl

I. 61

R = isobutyl

10

A wide variety of monomers according to the present invention can be prepared according to synthetic methods described in US 6,100,417, US 5,942,638, US 5,939,576, US 5,589,562, US 5,484,867, US 5,412,053, in the above mentioned reviews published by R. Baney et al. in Chemical Review, 1995, 95, 1409-1430 and by Guizhi Li et

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al. in Journal of Inorganic and Organometallic Polymers, Vol. 11  
(3), September 2001, page 123-154.

We will now describe systematically the principal other ingredients  
of the ink composition according to the present invention.

### Initiators

In a preferred embodiment, the initiator is a photoinitiator. The  
photoinitiators can be divided in compounds that are suited for  
cationic polymerization and compounds suited for free radical  
polymerization.

References on photoinitiators include following : P.K.T. Oldring  
(ed.), "Chemistry and Technology of UV and EB Formulation for  
Coatings, Inks and Paints: Vol. 3 "Photoinitiators for Free Radical  
and Cationic Polymerization," SITA Technology Ltd., London, UK  
(1991); N.S. Allen, "Photoinitiators for UV and visible curing of  
coatings: mechanism and properties", *Journal of Photochemistry and  
Photobiology, A: Chemistry* 100 (1996) 101-107; J.V. Koleske, "A  
radiation-cure primer", *Journal of Coatings Technology*, Vol69, No.  
866, March 1997, 29-38.

Disclosures specific on photoinitiators for cationic polymerisation  
include : J.V. Crivello, "The Chemistry of Photoacid Generating  
Compounds", *Proceedings of the ACS Division of Polymeric Materials:  
Science and Engineering*, Vol. 61, pages 62-66, (1989);  
J.V. Crivello and J.H.W. Lam, "Complex Triarylsulfonium Salt  
Photoinitiators I. The Identification, Characterization, and  
Synthesis of a New Class of Triarylsulfonium Salt Photoinitiators,"  
*Journal of Polymer Science, Polymer Chemistry Edition*, Vol. 18,  
2677-2695 (1980); J.V. Crivello and J.H.W. Lam, "Complex  
Triarylsulfonium Photoinitiators II. The Preparation of Several New  
Complex Triarylsulfonium salts and the Influence of Their Structure  
in Photoinitiated Cationic Polymerization," *Journal of Polymer  
Science, Polymer Chemistry Edition*, Vol. 18, pages 2697-2714 (1980);  
J.V. Crivello and J.H.W. Lam, "Diaryliodonium Salts A New Class of  
Photoinitiators for Cationic Polymerization," *Macromolecules*, Vol.



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10, pages 1307-1315 (1977); and J.V. Crivello, J.L. Lee and D.A. Conlon, "Developments in the Design and Applications of Novel Thermal and Photochemical Initiators for Cationic Polymerization", *Makromol. Chem. Macromolecular Symposium*, Vol. 13/14, pages 134-160 (1988).

Particularly preferred are the diaryl iodonium salts and their derivatives, the triaryl sulfonium salts and their derivatives, and the triphenyl phosphonium salts and their derivatives, with examples of alkyl and aryl substituents. Very recently, there have been described new types of photoinitiators for cationic polymerization such as triarylsulphonium-tetrakis(pentafluorophenyl)-borate (RHODORSIL 2074, Rhône-Poulenc Chimie), by C. Priou et al. in the Conference Proceedings of Radtech Europe '97, p. 314, and such as onium salts with specific light absorption characteristics in WO 97/47660 (Nippon Kayaky KK).

Useful photoinitiators for free radical polymerization are e.g. LUCIRIN LR8953 (ex BASF), IRGACURE 819 and 907 (ex Ciba-Geigy), DAROCUR 4865 (ex Ciba-Geigy), and isopropylthioxanthenes, e.g. QUANTACURE ITX (ex Rahn AG). Other useful photoinitiators for free radical polymerization are polymeric, oligomeric, respectively copolymerizable photoinitiators such as discussed by M. Visconti et al. respectively W. Davies et al. in the Conference papers 6, respectively 7, of the Radcure Coatings and Inks, Curing and Performance Conference (Harrogate, 22-23 June 1998). Such photoinitiators are e.g. ESACURE KIP150, ESACURE KT 37 and KT 55 (ex Lamberti), and acrylated IRGACURE 2959 or IRGACURE 2959 modified melamine acrylate (ex Ackros Chemicals).

Additional examples of suitable initiators are disclosed in following patents : U.S. Pat. Nos. 4,683,317, 4,378,277, 4,279,717, 4,480,368, 4,443,495, 4,303,924, 4,751,102, 4,334,970, 5,270,368, 5,395,724, and EP 0 540 203, EP 0 568 607 and EP 0 659 039.

Sometimes, it is also desirable to include, as well as a primary photoinitiator, a co-initiator, also called initiator synergist which is preferably of the amine type, e.g. the aminobenzoate type. The latter types of co-initiators are generally being used with the benzophenone or xanthone/thioxanthone types of primary

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photoinitiator. More examples can be found in the Oldring reference cited above. Apart from curing with UV-light, visible light curing systems can also be used, using for example the camphoroquinone dimethylaminoethylmethacrylate (DMAEMA) system.

- 5 The photoinitiator and occasionally the co-initiator are preferably present in an amount from 0.2 to 20 % by weight and most preferably between 1 and 10 %.

### Colorants

10

Inks of the present invention preferably contain a colorant. Any colorant may be used to impart the desired color to the ink. In embodiments of the present invention the colorant may include at least one pigment, one dye, or a combination thereof.

- 15 A wide variety of organic and inorganic dyes and pigments, alone or in combination may be selected for use in the ink compositions of this invention. The pigment particles should be sufficiently small to permit free flow of the ink through the ink jet printing device, especially at the ejecting nozzles that usually have a diameter  
20 ranging from 10  $\mu\text{m}$  to 50  $\mu\text{m}$ . The pigment particle size also has an influence on the pigment dispersion stability, which is critical throughout the life of the ink. It is also desirable to use small particles for maximum color strength.

- Accordingly, the average particle diameter may be from about 0.005  $\mu\text{m}$  to about 15  $\mu\text{m}$ . Preferably, the pigment particle size may range  
25 from about 0.005 to about 5  $\mu\text{m}$ , more preferably from about 0.005 to about 1  $\mu\text{m}$ , and most preferably from about 0.005 to about 0.3  $\mu\text{m}$ . Pigment particle sizes outside these ranges may, of course, be used as long as the objectives of the present invention are achieved.

- 30 Very fine dispersions of pigments and methods for their preparation are disclosed in e.g. EP 0 776 952, US 5,538,548, US 5,443,628, EP 0 259 130, US 5,285,064, EP 0 429 828, and EP 0 526 198.

- The pigment can be black, cyan, magenta, yellow, red, blue, green, brown, mixtures thereof, and the like. For example, suitable pigment  
35 materials include carbon blacks such as Regal 400R, Mogul L, Elftex 320 from Cabot Co., or Carbon Black FW18, Special Black 250, Special

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Black 350, Special Black 550, Printex 25, Printex 35, Printex 55, Printex 150T from Degussa Co., and Pigment Black 7. Additional examples of suitable pigments are disclosed in, for example, U.S. Pat. No. 5,389,133 to Gundlach et al..

- 5 Suitable pigments include, for instance, C. I. Pigment Yellow 17, C. I. Pigment Blue 27, C. I. Pigment Red 49:2, C. I. Pigment Red 81:1, C. I. Pigment Red 81:3, C. I. Pigment Red 81:x, C. I. Pigment Yellow 83, C. I. Pigment Red 57:1, C. I. Pigment Red 49:1, C. I. Pigment Violet 23, C. I. Pigment Green 7, C. I. Pigment Blue 61, C. I.
- 10 Pigment Red 48:1, C. I. Pigment Red 52:1, C. I. Pigment Violet 1, C. I. Pigment White 6, C. I. Pigment Blue 15, C. I. Pigment Yellow 12, C. I. Pigment Blue 56, C. I. Pigment Orange 5, C. I. Pigment Black 7, C. I. Pigment Yellow 14, C. I. Pigment Red 48:2, C. I. Pigment Blue 15:3, C. I. Pigment Yellow 1, C. I. Pigment Yellow 3, C. I.
- 15 Pigment Yellow 13, C. I. Pigment Orange 16, C. I. Pigment Yellow 55, C. I. Pigment Red 41, C. I. Pigment Orange 34, C. I. Pigment Blue 62, C. I. Pigment Red 22, C. I. Pigment Red 170, C. I. Pigment Red 88, C. I. Pigment Yellow 151, C. I. Pigment Red 184, C. I. Pigment Blue 1:2, C. I. Pigment Red 3, C. I. Pigment Blue 15:1, C. I. Pigment
- 20 Blue 15:3, C. I. Pigment Blue 15:4, C. I. Pigment Red 23, C. I. Pigment Red 112, C. I. Pigment Yellow 126, C. I. Pigment Red 169, C. I. Pigment Orange 13, C. I. Pigment Red 1-10, 12, C. I. Pigment Blue 1:X, C. I. Pigment Yellow 42, C. I. Pigment Red 101, C. I. Pigment Brown 6, C. I. Pigment Brown 7, C. I. Pigment Brown 7:X, C. I.
- 25 Pigment Black 11, C. I. Pigment Metal 1, C. I. Pigment Metal 2, C. I. Pigment Yellow 128, C. I. Pigment Yellow 93, C. I. Pigment Yellow 74, C. I. Pigment Yellow 138, C. I. Pigment Yellow 139, C. I. Pigment Yellow 154, C. I. Pigment Yellow 185, C. I. Pigment Yellow 180, C. I. Pigment Red 122, C. I. Pigment Red 184, bridged aluminum
- 30 phtalocyanine pigments and solid solutions of pigments.
- Furtheron the pigment may be chosen from those disclosed in *Industrial Organic Pigments, Production, Properties, Applications*, second edition, W. Herbst, K. Hunger ; VCH, 1997.
- Most preferred pigments are Pigment Yellow 1, 3, 128, 109, 93, 17, 14, 10, 12, 13, 83, 65, 75, 74, 73, 138, 139, 154, 151, 180, 185;
- 35 Pigment Red 122, 22, 23, 17, 210, 170, 188, 185, 146, 144, 176,

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57:1, 184, 202, 206, 207; Pigment Blue 15:3, Pigment Blue 15:2, Pigment Blue 15:1, Pigment Blue 15:4, Pigment Blue 15:6, Pigment Blue 16; carbon black.

The pigment may, but need not, be in the form of a dispersion  
5 comprising a dispersant also called pigment stabilizer. The latter may be, for example, of the polyester, polyurethane or polyacrylate type, especially in the form of high molecular weight block copolymer, and would typically be incorporated at 2.5% to 100% by weight of the pigment. Suitable examples are DISPERBYK (ex BYK  
10 Chemie) or SOLSPERSE (ex Zeneca) dispersants. A detailed list of non-polymeric as well as some polymeric dispersants appears in, for example, McCutcheon's Functional Materials, North American Edition, Manufacturing Confectioner Publishing Co., Glen Rock, N.J., pp. 110-129 (1990).

15 Other pigment stabilizers are disclosed in DE 19636382, US 5,720,802, US 5,713,993, PCT/GB95/02501, US 5,085,689 and GB 2303376.

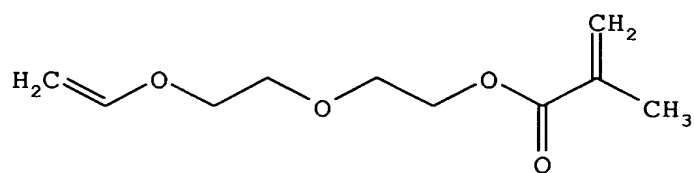
The pigment or dye may be present in the ink composition in any effective amount, generally from about 0.5 to about 20 percent by  
20 weight of the ink.

**Other monomers, oligomers or reactive diluents usable in combination with the invention monomers**

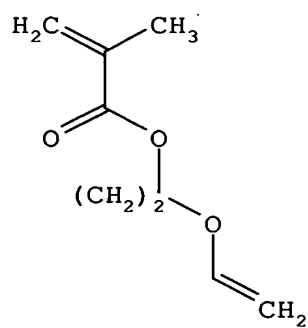
25 A wide variety of photopolymerisable and photocrosslinkable compounds can be used in combination with the monomers of the present invention.

Suitable monomers include e.g. the monomers disclosed in DE-OS Nos. 4005231, 3516256, 3516257, 3632657 and US 4,629,676, US 6,294,592  
30 and WO 97/31071 and US 6,300,388. The monomers of the present invention are preferably used in combination with vinyl ether methacrylates or vinyl ether acrylates such as described in US 6,310,115. Representative examples of such compounds are given in Table 2.

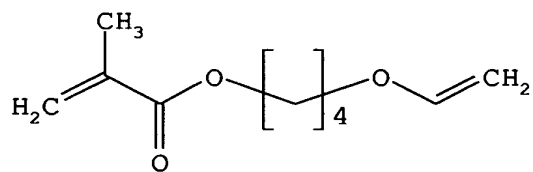
- 25 -

Table 2. Vinylether(meth)acrylates

5 II.1

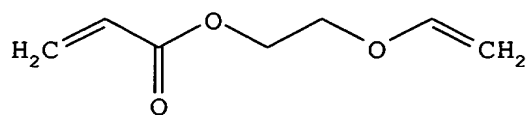


II.2

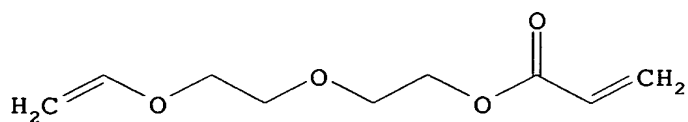


10

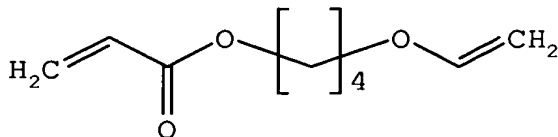
II.3



15 II.4



II.5



## II.6

The photopolymerizable composition may also comprise polymers, conducting or semiconducting polymers, prepolymers and/or oligomers and/or reactive diluents comprising one or more polymerizable functions.

Suitable prepolymers and reactive diluents for use in radiation curable compositions such as the ink composition of the present invention may be selected from the group consisting of unsaturated urethane(meth)acrylates, epoxy(meth)acrylates, polyolacrylates, polyether(meth)acrylates and polyester(meth)acrylates as described e.g. in "Chemistry & Technology of UV and EB formulation for coatings, inks and paints" Vol.2 : Prepolymers and Reactive diluents for UV and EB curable formulations." Ed. G. WEBSTER - SITA Technology - London (1996).

A survey of UV-curable coating compositions is given e.g. in the periodical "Coating" 9/88, p. 348-353.

Other usable prepolymers and oligomers belong to the class of aliphatic and aromatic polyester-urethane acrylates. The structure of polyester-urethane acrylates is given in the booklet "Radiation Cured Coatings" by John R. Constanza, A.P. Silveri and Joseph A. Vona, published by Federation of Societies for Coatings Technology, 1315 Walnut St. Philadelphia, PA 19107 USA (June 1986) p. 9.

It will be clear that all these cited monomers, prepolymers, polymers and oligomers can be used in admixture.

A preferred second oligomer used in combination with a monomer of the present invention is an amino modified polyether acrylate known as CN 501 from Cray Valley Co..

In a particular embodiment the second monomer, oligomer or prepolymer not belonging to the invention is the principal compound

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involved in the radiation curing, and the monomer according to the invention functions as so-called "reactive diluent" in order to reduce the viscosity of the final ink formulation.

## 5 Other additives

Inks of the present invention may include additives such as biocides, buffering agents, anti-mold agents, pH adjustment agents, electric conductivity adjustment agents, chelating agents, anti-  
10 rusting agents, polymerisation inhibitors, light stabilizers, antioxidants and the like. Such additives may be included in the ink jet inks of the present invention in any effective amount, as desired.

Examples of pH controlling agents suitable for inks of the present  
15 invention include, but are not limited to, acids, and bases, including hydroxides of alkali metals such as lithium hydroxide, sodium hydroxide and potassium hydroxide. The amount included will depend, of course, on the specific component being included. Furtheron, the ink composition of the present invention may also  
20 comprise surfactants and photoinitiator stabilizers. Suitable photoinitiator stabilizers include those disclosed in EP 0 465 039. Suitable surfactants are preferably of the non-ionic type, for example FLUORAD FC430 (ex 3M Corp.). Such surfactants when present are preferably included in an amount of 0.1% to 10% by weight of the  
25 total composition.

Compositions according to the present invention may contain water and/or organic solvents, such as alcohols, fluorinated solvents and dipolar aprotic solvents. Preferable solvents are methanol, ethanol, propanol, 1-butanol, 1-pentanol, 2-butanol, t.-butanol, glycol,  
30 glycolethers, N-methylpyrrolidone, N,N-dimethylacetamid, N, N-dimethylformamid, 2,4-pentanedione and hexafluoroacetone are used. The ink compositions of the present invention may further comprise conducting or semiconducting polymers, such as polyanilines, polypyrroles, polythiophenes such as poly(ethylenedioxythiophene)  
35 (PEDOT), substituted or unsubstituted poly(phenylenevinylenes) (PPV's) such as PPV and MEH-PPV, polyfluorenes such as PF6, etc.

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The ink compositions of the present invention may further comprise a dendrimer.

Dendrimers are radially symmetrical molecules of a STARBURST™.

topology comprised of an initiator core, such as nitrogen,

5 ethyleneimine, and the like, interior layers attached to the core

and comprised of a suitable number of arms, for instance, two to

four arms, each arm being comprised of repeating units with the

number of repeating units in each arm being considered the

generation of the dendrimer, and terminal groups functionality, such

10 as, for example, a primary amine attached to the outmost generation,

which dendrimers are illustrated, for example, in U.S. Pat. Nos.

4,507,466, 4,631,337, 4,558,120, 4,568,737, and 4,587,329, and in

Tomalia et al., *Angewandte Chemie, Int. Ed. Engl.* 29, 138 (1990).

The size and shape of the STARBURST™ dendrimer molecule and the

15 functional groups present in the dendrimer molecule can be

controlled by the choice of the initiator core, the number of

generations, and the choice of repeating units employed at each

generation.

The choice of the dendrimer components can affect the properties of

20 the dendrimers. The initiator core type can affect the dendrimer

shape producing, for example, spheroid-shaped dendrimers,

cylindrical- or rod-shaped dendrimers, or ellipsoid-shaped

dendrimers. Sequential building of generations determines the

dimensions of the dendrimers and the nature of its interior.

25 Examples of suitable core materials include ammonia, polyfunctional

alcohols, such as pentaerythritol or tris-(hydroxymethyl)ethane,

1,1,1-tris-(4'-hydroxyphenyl)ethane, polyfunctional amines, such as

ethylene diamine, linear polyethyleneimines, and the like. The

chemical functionality of the repeating unit in the interior layers

30 can include, for example, amidoamines, such as aminoethyl acetamide,

imines, such as diethylene diimine, or ethers like those obtained

from materials such as, for example, 3,5-dihydroxyethyl benzyl

alcohol. The terminal functionalities include, for example, amino

groups, hydroxyl groups, carboxylic acid groups, carboxylates,

35 esters, amides, phosphates, sulfonates, and the like. The synthesis

of dendrimers usually occurs by a divergent approach that involves



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the initial reaction of a monomer with the initiator core, followed by exhaustive reaction of the resulting functional groups with a difunctional compound, such as a diamine, including, for example, ethylene diamine, to afford the next generation of reactive amino groups. Thus, for example, ethylene diamine can be suitably reacted first with methyl acrylate to produce a compound such as N,N,N',N'-tetra(methoxycarbonylethyl)ethylene diamine. The aforesaid compound can be reacted in the next step with ethylene diamine to produce an amidoamine dendrimer having a generation number of zero, a molecular weight of 517, and four primary amino groups at the surface. Repetition of the above two-step procedure leads to subsequent generations.

An alternate synthetic route uses a convergent growth synthesis as described in detail in Hawker et al., *J. Amer. Chem. Soc.*, 112, 7638 (1990).

The dendrimer may have other groups or segments, in addition to amino groups. For instance, the dendrimer may have a dye covalently attached to it, or it may have certain functional groups grafted onto it. Preferred dendrimers for use in the preparation of the ink composition of the present invention include the dendrimers disclosed in US 6,312,679.

The dendrimers may be grafted with, for example, alkylene oxide oligomers or polymers, wherein the alkylene has 1-12 carbon atoms and the degree of polymerization of the alkylene oxide is in the range of from about 2 to about 100. The amount of grafting can be in any suitable range, preferably below 50% of the amino groups, and even more preferably below 10% of the amino groups. Grafting of ethylene oxide on the dendrimer can be performed by any suitable means known to those of ordinary skill in the art. For instance, a polyethylene glycol monomethyl ether of suitable molecular weight can be converted to polyethylene glycol monomethyl ether p-toluene sulfonate by suitably reacting with p-toluenesulfonyl chloride and pyridine, and the sulfonate then reacted with the dendrimer under suitable conditions, as known to those of ordinary skill in the art. Grafted dendrimers can also be obtained from Dendritech, Inc. in Midland, Mich.

- 30 -

Other preferred dendrimers for use in the preparation of the ink composition of the present invention include those having terminal amine functionality at the surface. It is further preferred that the dendrimer has a molecular weight in the range from about 300 to about 100,000, a generation number of from 0 to 10, a surface amine group concentration of from about 3 to about 4100, and a molecular diameter of from about 1 nm to about 1000 nm. More preferred dendrimers are those having terminal primary amine functionality. It is also more preferred that the dendrimer has a molecular weight in the range from about 500 to about 30,000, a generation number of from 0 to about 5, a surface group concentration of from about 4 to about 150, and a molecular diameter of from about 1 nm to about 150 nm. It is also preferred that the polydispersity index ( $M_w/M_n$ ) of the dendrimer is low, preferably in the range of from about 1.1000 to about 1.0001, and more preferably in the range of from about 1.001 to about 1.0001. Examples of dendrimers prepared by the divergent approach include the STARBURST™ dendrimers available from Dendritech, Inc. These dendrimers from Dendritech, Inc. are polyamidoamines (PAMAMs) having primary amine terminal surface functionality, and made of ethylene diamine core and sequenced copolymers of ethylene diamine and methyl acrylate. They have a polydispersity index of 1.0007.

The dendrimer is present in the ink composition in an amount sufficient to provide sufficient adhesion of the ink components to the printing surface, and also to provide sufficient water resistance and cold and hot humidity resistance. The amount of the dendrimer is preferably in the range of from about 0.1% to about 10% by weight, more preferably in the range of from about 0.5% to about 2% by weight, and even more preferably in the range of from about 1% by weight to about 2% by weight, of the ink composition.

In formulating the final ink jet ink compositions of the present invention, certain physical properties should be satisfied. For example, ink compositions for use in ink jet recording processes should have appropriate viscosity and surface tension

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characteristics. In the present invention, it is preferred that the ink jet ink composition has a viscosity of from about 1 to about 100 mPa.s at 25 °C. The surface tension is preferably from 20 to 72 mN/m and most preferably from 20 to 60 mN/m.

5

Apparatuses for radiation curing are known to those skilled in the art and are commercially available. For example, the curing proceeds with medium pressure mercury vapour lamps with or without electrodes, or pulsed xenon lamps. These ultraviolet sources usually  
10 are equipped with a cooling installation, an installation to remove the produced ozone and optionally a nitrogen inflow to exclude air from the surface of the product to be cured during radiation processing. An intensity of 40 to 240 W/cm in the 200-400 nm region is usually employed. An example of a commercially available  
15 ultraviolet medium-pressure electrodeless mercury vapour lamp is the model VPS/I600 curing system of Fusion UV systems Ltd., UK. A pulsed xenon flash lamp is commercially available from IST Strahlentechnik GmbH, Nürtingen, Germany. Using the Fusion model one has also the possibility to use metal halide doped Hg vapour or XeCl excimer  
20 lamps, each with its specific UV emission spectrum. This permits a higher degree of freedom in formulating the curing composition : a more efficient curing is possible using the lamp with the most appropriate spectral characteristics.

High energy ionizing radiation such as X-rays, gamma rays, beta rays  
25 and accelerated electrons can also be used to accomplish curing of the ink composition.

The inks according to the present invention can be used with any ink jet printhead. The inks of the present invention are preferably used with piezoelectric printheads which can be heated to accomodate  
30 different viscosities. Typical examples include printheads form Spectra Inc., Epson, Brother, Xaar Ltd., Trident International, as well as printhead designs described in "Inkjet Technology and Product Development Strategies, S.F. Pond, Torrey Pines research, 2000" and in "Proceedings IS&T's International Conference on Digital  
35 Production Printing and Industrial Applications", 2001, Antwerp, Belgium, such as page 230-234. The inks can be used with any type of

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nozzle plate, such as nozzle plates based on silicon, polyimide, silicon nitride.

5 The ink jet receiver materials to which the ink composition of the present invention can be jetted are not limited and include e.g. paper, coated paper, polyolefin coated paper, cardboard, wood, composite boards, plastic, coated plastic, canvas, textile, metal, glasses, plant fibre products, leather, and ceramics.

10 The inks according to the present invention can also be used in other printing applications where radiation curing is applied, such as flexo printing and liquid electrophotography.  
The inks according to the present invention can also be used to manufacture printing plates, such as in computer-to-plate  
15 applications, and to make printed circuit boards (PCB).

The present invention will now be illustrated by the following examples without however being limited thereto.

20

## EXAMPLES

### Example 1. Solubility

25 The solubility of some invention compounds was determined in several reactive diluents and oligomers such as TPGDA, DPGDA, TMPTA, CN501 (an amino modified polyether acrylate from Cray Valley Co.).

Invention Compounds I.10, I.22 and I.24 were soluble at 50wt% in  
30 TPGDA, TMPTA and CN501.

Invention Compounds I.6 and I.7 were soluble below 10wt% in TPGDA, TMPTA and CN501. Addition of a very small amount of solvent ( $\text{CH}_2\text{Cl}_2$ ) resulted in complete solubility and remained so upon removal of the solvent.

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Invention Compound I.9 was not soluble but dissolved in TPGDA and TMPTA after the addition of a very small amount of solvent ( $\text{CH}_2\text{Cl}_2$ ). Invention Compound I.9 was not soluble in CN501 in which it formed a milky white solution.

5

Example 2. Clear inks.

The following clear inks were formulated :

10 Table 3:

|        | <b>DPGDA</b> | <b>Craynor CN501</b> | <b>I.10</b> |
|--------|--------------|----------------------|-------------|
| ink 1  | 50 g         | 45 g                 | 5 g         |
| ink 2  | 50 g         | 40 g                 | 10 g        |
| ink 3  | 50 g         | 25 g                 | 25 g        |
|        | <b>DPGDA</b> | <b>Craynor CN501</b> | <b>I.24</b> |
| ink 4  | 50 g         | 45 g                 | 5 g         |
| ink 5  | 50 g         | 40 g                 | 10 g        |
| ink 6  | 50 g         | 25 g                 | 25 g        |
|        | <b>DPGDA</b> | <b>Craynor CN501</b> | <b>I.22</b> |
| ink 7  | 50 g         | 45 g                 | 5 g         |
| ink 8  | 50 g         | 40 g                 | 10 g        |
| ink 9  | 50 g         | 25 g                 | 25 g        |
|        | <b>DPGDA</b> | <b>Craynor CN501</b> | <b>I.6</b>  |
| ink 10 | 50 g         | 47.5 g               | 2.5 g       |
| ink 11 | 50 g         | 45 g                 | 5 g         |
|        | <b>DPGDA</b> | <b>Craynor CN501</b> | <b>I.7</b>  |
| ink 12 | 50 g         | 47.5 g               | 2.5 g       |
| ink 13 | 50 g         | 45 g                 | 5 g         |

To each ink 10 g Irgacure 500 and 5 g NMDA were added.

15 Each ink composition was coated on a clear unsubbed 175  $\mu\text{m}$  thick PET polyester film, using a bar coater and a 10 $\mu\text{m}$  wired bar. The coated films were placed on a conveyer belt and transported underneath a UV

- 34 -

lamp. A Fusion DRSE-120 conveyer, equipped with a Fusion VPS/I600 lamp (D bulb), was used to cure the coated inks. A conveyor belt speed of 20 m/min was used. The percentage of the maximum output of the lamp to cure the film was used as a measure for sensitivity. A  
5 sensitivity above 100 means slowing down the transport belt to 10 m/min, measuring the percentage of the maximum output and multiplying it by 2. The curing was evaluated by means of a scratch test with a cotton bud. When the coating did not remain visually unchanged after scratching, the curing was not complete. The  
10 sensitivities of the inks are summarised in Table 4.

Table 4

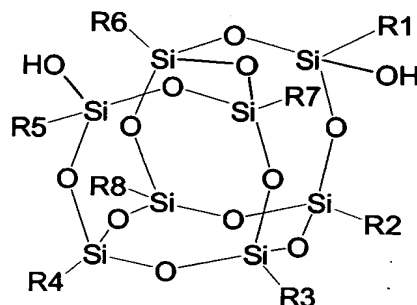
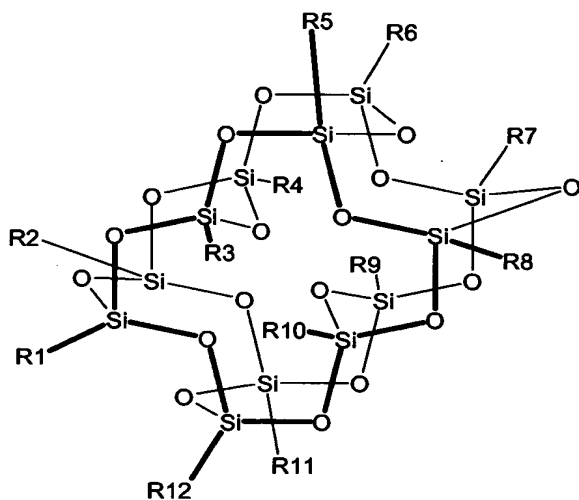
|        | Sensitivity output % |
|--------|----------------------|
| Ink 1  | 55                   |
| Ink 2  | 65                   |
| Ink 3  | 100                  |
| Ink 4  | 60                   |
| Ink 5  | 90                   |
| Ink 6  | 100                  |
| Ink 7  | 50                   |
| Ink 8  | 60                   |
| Ink 9  | 90                   |
| Ink 10 | 50                   |
| Ink 11 | 50                   |
| Ink 12 | 50                   |
| Ink 13 | 45                   |

15 As can be seen from Table 4 all inks are readily cured.

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I

II



III

IV

wherein

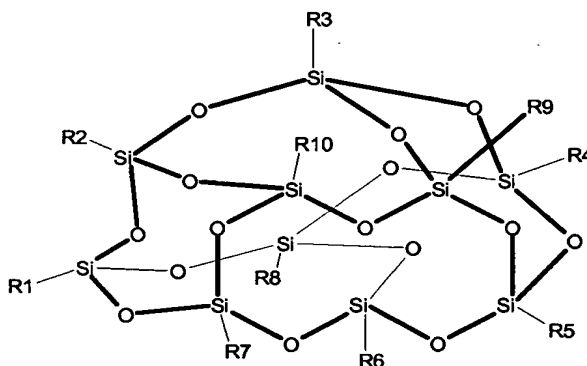
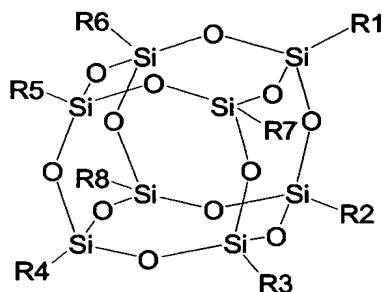
R1 to R12 represent hydrogen, inorganic or organic substituents; at least one of the R1-R12 groups comprises a curable functional group, preferably an epoxide, an aziridine, an acrylate, a methacrylate, an acrylamide, a methacrylamide, an olefinic group, a styryl group.

4. A radiation curable ink composition according to any of claims 1 to 3 wherein said composition is cured radically.
5. A radiation curable ink composition according to any of claims 1 to 3 wherein said composition is cured cationically.
6. A radiation curable ink composition according to any of claims 1 to 5 wherein said composition further contains a colorant.

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**[CLAIMS]**

1. A radiation curable ink composition comprising one or more silsesquioxanes represented by the following empirical formula  $\text{RSiO}_{1.5}$ , wherein R represents hydrogen, inorganic or any alkyl group, alkylene group, aryl group, arylene group, or organo-functional derivatives of alkyl, alkylene, aryl or arylene groups.
2. A radiation curable ink composition according to claim 1 comprising one or more radiation curable polyhedral oligomeric silsesquioxanes (POSS) represented by the following empirical formula  $[\text{R}(\text{SiO}_{1.5})]_n$  wherein  $n=4,6,8,10,12,14,16$  and larger, and where R represents hydrogen, inorganic or organic substituents. At least one R-group comprises a curable functional group, preferably an epoxide, an aziridine, an acrylate, a methacrylate, an acrylamide, a methacrylamide, an olefinic group, a styryl group.
3. A radiation curable ink composition according to claim 2 comprising one or more radiation curable polyhedral oligomeric silsesquioxanes (POSS), represented by the following empirical formula  $[\text{R}(\text{SiO}_{1.5})]_n$  wherein  $n=4,6,8,10,12,14,16$  and larger, that have specific cage structures as represented by formulae I to III or partial cage structures as represented by formula IV:





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15. A radiation curable ink composition according to any of claims 1 to 14 wherein the viscosity of said ink composition is comprised between 1 and 100 mPa.s at 25 °C.
- 5 16. A radiation curable ink composition according to any of claims 1 to 15 wherein said composition further contains water as a solvent.
17. A radiation curable ink composition according to any of claims 1 to 16 wherein said composition further contains an organic solvent.
- 10 18. A radiation curable ink composition according to any of claims 1 to 17 further comprising a dendrimer.
19. A radiation curable ink composition according to any of claims 1 to 18 further comprising conducting or semiconducting polymers.
- 15 20. A radiation curable ink composition according to claim 19 wherein said conducting or semiconducting polymers are chosen from the group consisting of substituted or unsubstituted polyanilines, polypyrroles, polythiophenes, poly(phenylenevinylenes) or polyfluorenes.
- 20 21. A radiation curable ink composition according to any of claims 1 to 20 further comprising an antioxidant.
22. A radiation curable ink composition according to any of claims 1 to 21 comprising one or more vinylether acrylates or vinylether methacrylates.
- 25 23. A radiation curable ink composition according to claim 22 wherein the vinylether acrylates or vinylether methacrylates are chosen from the following structures:

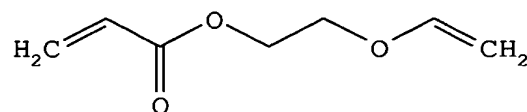
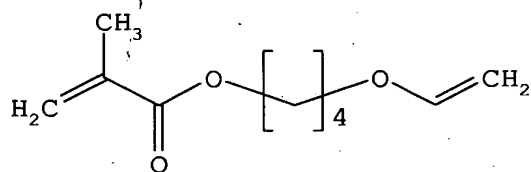
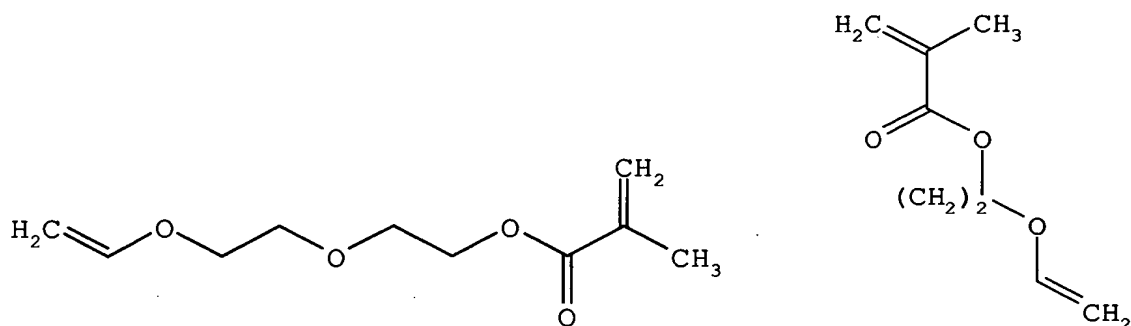
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7. A radiation curable ink composition according to claim 6 wherein said colorant is a dispersed pigment or a solid solution of a pigment.
8. A radiation curable ink composition according to claim 7 wherein  
5 said pigment is chosen from the list consisting of Pigment Yellow 1, 3, 128, 109, 93, 17, 14, 10, 12, 13, 83, 65, 75, 74, 73, 138, 139, 154, 151, 180, 185; Pigment Red 122, 22, 23, 17, 210, 170, 188, 185, 146, 144, 176, 57:1, 184, 202, 206, 207; Pigment Blue 15:3, Pigment Blue 15:2, Pigment Blue 15:1, Pigment Blue 15:4,  
10 Pigment Blue 15:6, Pigment Blue 16, or carbon black.
9. A radiation curable ink composition according to claim 6 wherein said colorant is a soluble dye.
10. A radiation curable ink composition according to any of claims 1  
15 to 9 wherein said composition further contains an inorganic pigment.
11. A radiation curable ink composition according to any of claims 1 to 10 wherein said composition further contains a photoinitiator or a mixture of photoinitiators.
12. A radiation curable ink composition according to claim 11 wherein  
20 said composition further contains an initiator synergist.
13. A radiation curable ink composition according to any of claims 1 to 12 wherein said ink composition further contains a second photopolymerizable monomer, oligomer or prepolymer.
14. A radiation curable ink composition according to claim 13 wherein  
25 said second monomer is chosen from the group consisting of following chemical classes: an amino modified polyether acrylate, an urethane acrylate, a polyester acrylate, a polyether acrylate, and an epoxy acrylate.

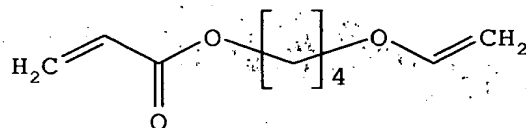
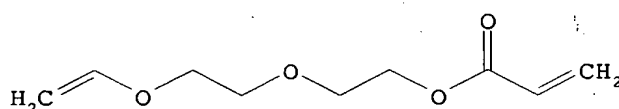
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27. A process according to claim 26 wherein said ink accepting layer contains a microporous pigment or a polymer blend.

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24. A process for obtaining a colorless, monochrome or multicolour ink jet image comprising the steps of jetting one or more streams of ink droplets having a composition according to any of the previous claims to an ink jet recording element, and subjecting the obtained image to radiation curing.
25. A process according to claim 24 wherein said radiation curing is performed by means of one or more ultra-violet sources or electron beam sources.
26. A process according to claim 24 or 25 wherein said ink jet recording element is chosen from the group consisting of paper, coated paper, polyolefin coated paper, cardboard, wood, composite boards, plastic, coated plastic, canvas, textile, metal, glasses, plant fibre products, leather, magnetic materials and ceramics, or supports carrying an ink-accepting layer.